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(54) Durable, antistatic, soil release agents and their application to substrates

(57) A durable, antistatic soil release agent which is resistant to yellowing on the substrate has the formula

$$X \begin{matrix} (Y_1)_a \\ | \\ | \\ (Y_2)_b \end{matrix} (Y_3)_c \quad \text{wherein}$$
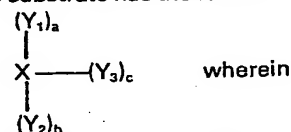
X is an aminoplast resin moiety having 4 to 6 methylene groups, each of which is attached to an amino nitrogen atom and to Y_1, Y_2 or Y_3;
Y_1 is $O(C_2H_4O)_{5-20}R_1$ wherein R_1 is C_{1-5} alkyl;
Y_2 is $O(C_2H_4O)_{5-88}R_2$ wherein R_2 is C_{6-20} alkyl;

$$Y_3 \text{ is } [(OC_2H_4)_m \overset{R_3}{\underset{R_4}{N}} (C_2H_4O)_n H \quad A^\ominus]$$
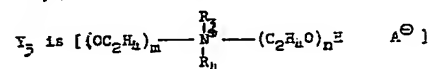
wherein R_3 is C_{4-20} alkyl, C_{4-20} alkenyl or benzyl, R_4 is C_{1-4} alkyl, A^- is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;
each of a and b is 0 to 2 and the sum of a and b is 1 to 2;
c is 1 to 2;
the sum of a, b and c is 1 to 4;
said agent having a specified calculated hydrophile-lipophile balance (HLB), viscosity, electrical resistivity (initially and after 10 washes) and soil release rating on polyester fabric.
It is applied by
(a) diluting the agent,
(b) adding a metal or an ammonium salt to achieve a cloud point of less than 100°C but greater than 25°C, and/or adding sufficient polyacidic compound having a second dissociation constant of greater than 1×10^{-8} to achieve a pH of 3.0 to 6.0,
(c) applying the diluted agent of step (b) to the substrate, and
(d) drying and curing the agent on the substrate.

SPECIFICATION

### Application of durable, antistatic, soil release agents to substrates

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This invention relates to a chemical composition which is useful for imparting durable antistatic and soil release characteristics to a wide variety of subs-trates, for example, textile fabrics, to a process for
10 durably applying the composition to a substrate, and to substrate durably treated with the chemical composition.
It is an object of this invention to provide a chemical composition which can be used to impart dur-
15 able, antistatic, soil release and, to some extent, anti-soil redeposition characteristics to a substrate treated therewith. Another object is to provide a process by which the composition can be durably applied to the substrate. A further object is to pro-
20 vide a substrate which exhibits durable, antistatic, soil release and, to some extent, anti-soil redeposition properties. Still another object is to provide such a composition and process which are particularly useful in the textile trade.
25 Extensive prior art exists in the fields of antistatic agents and soil release agents. Such materials are used extensively to impart antistatic and soil release characteristics to substrates treated therewith, particularly textile materials, such as textile fabrics. A
30 desirable feature of such agents is durability, that is, the ability of the agent to be retained on the substrate during subsequent handling or use thereof. For example, in the case of textile fabrics, such as clothing, it is desirable that any antistatic or soil release
35 property imparted to the fabric be retained thereon through subsequent laundering operations. A need exists for a single substrate treating agent or composition which can impart durable, antistatic soil release properties to the substrate.
40 The invention resides in a durable antistatic soil release agent which is resistant to yellowing on the substrate treated therewith, to the method of applying the agent to the substrate, and to substrate treated with the agent which is of the formula
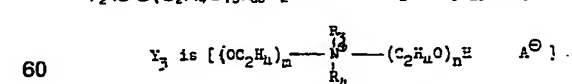45
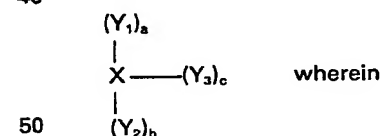
$$\begin{array}{c} (Y_1)_a \\ | \\ X \!\!-\!\!-\!\!-\!\!(Y_3)_c \qquad \text{wherein} \\ | \\ (Y_2)_b \end{array}$$

50

X is an aminoplast resin moiety having amino nit-rogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nit-
55 rogen atom and to Y_1, Y_2 or Y_3;
Y_1 is $O(C_2H_4O)_{5-20}R_1$ wherein R_1 is C_{1-5} alkyl;
Y_2 is $O(C_2H_4O)_{5-88}R_2$ wherein R_2 is C_{6-20} alkyl;

60
$$Y_3 \text{ is } [(OC_2H_4)_m \!\!-\!\! \overset{\overset{R_3}{|}}{\underset{\underset{R_4}{|}}{N}} \!\!-\!\! (C_2H_4O)_n^H \qquad A^\ominus]$$

wherein R_3 is C_{4-20} alkyl, C_{4-20} alkenyl or benzyl, R_4 is C_{1-4} alkyl, $A^\ominus$ is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12
65 to 100;

each of a and b is 0 to 2 and the sum of a and b is 0 to 2;
c is 1 to 2;
the sum of a, b and c is 1 to 4;
70 said agent having a calculated hydrophile - lipophile balance (HLB) of 14.5 to 18.0, a 20 weight% aqueous solution viscosity, as measured at 20°C on a Brookfield viscometer, of 250 to 16,000 cps (0.250 to 16.000 pascal seconds), an electrical resistivity (Keithley log
75 R) on polyester fabric, at 20 ± 2% relative humidity (R.H.) and 23 ± 1°C, of no greater than 13.00 initially and no greater than 14.25 after 10 washes, and a soil release rating on polyester fabric of at least 3 initially. Preferably, in the above formula, Y_1 is
80 $O(C_2H_4O)_{10-16}$ and R_1 is CH_3; Y_2 is $O(C_2H_4O)_{15-30}$ and R_2 is $C_{13}H_{27}$; in Y_3, R_3 is C_{8-18} alkyl, or C_{8-12} alkyl to achieve good water wettability (drop absorption), R_4 is CH_3, $A^\ominus$ is $\ominus OSO_3CH_3$ and m + n is 20 to 50; the HLB is 15.5 to 17.0; and the 20% aqueous viscosity is
85 2,000 to 8,000 cps (2.00 to 8.00 pascal seconds).
Although it will be described in greater detail hereinafter, the process of the invention resides in a process for applying the aforesaid agent to a substrate, which process comprises the steps:
90   (a)   diluting the agent with a normally liquid medium to achieve the desired application liquid viscosity,
(b)   adding sufficient salt of a mono-, di- or trivalent metal or of an ammonium cation to achieve a
95 cloud point, of the diluted agent of step (a), of less than 100°C but greater than 25°C, or adding sufficient polyacidic compound having a second dissociation constant of greater than 1 x 10⁻⁸ to achieve a pH, of the diluted agent of step (a), or 3.0 to 6.0, or adding
100 both said salt and said polyacidic compound to achieve said cloud point and pH,
(c)   applying the diluted agent of step (b) to the substrate to be treated so as to achieve the desired level of agent on the substrate,
105   (d)   drying and curing the agent on the substrate, and
(e)   recovering substrate which has been durably treated with the agent of the aforesaid formula.
Finally, the invention herein also resides in subs-
110 trate which has been durably treated with the aforesaid agent.
The agent of the invention is prepared by conventional techniques by contacting, in appropriate amounts, under appropriate reaction conditions,
115 appropriate precursors of the aforesaid moieties X and Y_3 and the optional moieties Y_1 and Y_2.
Exemplary of X moiety precursors which can be used to produce the agent of the invention are the melamine methylol derivatives having 4 to 6
120 methylol groups, which methylol groups can be ether capped with, for example C_{1-4} alkyl. The optional Y_1 and Y_2 moieties can be provided by the commonly available polyethylene oxides. For example, polyethylene glycol monoethers having 5 to
125 20 ethyleneoxy moieties and C_{1-5} alkyl ether end groups are commercially available under the Carbowax® designation, thus providing a source of the Y_1 moiety. Similarly, the Y_2 moiety is provided by commercially available materials, such as those
130 designated Merpol®, which are polyethylene glycol

monoethers having 5 to 88 ethyleneoxy moieties and C_{6-20} alkyl ether end groups.

General procedure used to prepare Y_2 precursor

One mole of the appropriate C_6-C_{20} alkyl alcohol is
5 dried to $\cong 0.2$ weight% water, either thermally under nitrogen purge or under reduced pressure (if the boiling point of the alcohol is high enough). About 0.5 part of sodium hydride (or a similar catalyst) is then added to the alcohol, with stirring, at 80-100°C,
10 under a nitrogen atmosphere. After 15-60 minutes of agitation, the temperature is increased. When the alcohol temperature is about 140°C, the nitrogen purge is stopped and ethylene oxide is introduced. The temperature is allowed to reach about 155°C.
15 The addition of ethylene oxide is continued at this temperature until a total of 5 to 88 moles (depending on the ethyleneoxide content desired) is added per mole of alcohol present. After addition and reaction of the ethylene oxide is complete, any sodium
20 alcoholate formed (from the sodium hydride) is neutralized at about 70°C with an equivalent amount of acid, such as p-toluenesulfonic acid. The finished product, if it is not used immediately, can be stored in a sealed container until needed.
25 *General procedure used to prepare Y_3 precursor*

One mole of the appropriate n-alkylamine is heated under a nitrogen purge to at least 120°C, preferably within the range 185 to 230°C. The nitrogen purge is discontinued and ethylene oxide is intro-
30 duced and reacted with the amine to produce N, N - bis - 2 - hydroxyethyl - n - alkyl amine according to the procedure of H. L. Sanders, J. B. Braunwarth, R. B. McConnell and R. A. Swenson, J. Am Oil Chem. Soc., *46* 167 (1969). The lower molecular weight bis - 2
35 - hydroxyethyl - n - alkylamines are commercially available. About 1 part of 50-60 weight% sodium hydride in oil is then added to the one mole of the bis - 2 - hydroxyethyl - n - alkylamine under a nitrogen purge at 50-100°C. The mixture is heated with agita-
40 tion under nitrogen to about 140°C. The nitrogen purge is discontinued, ethylene oxide is introduced and the reaction is run at 140-170°C, preferably at 155-165°C. Ethylene oxide addition is continued until the desired amount has reacted with the bis - 2 -
45 hydroxyethyl - n - alkylamine. Then nitrogen purging is resumed while the product is cooled to about 80°C. An amount of acid, such as dry p-toluenesulfonic acid, equivalent to the 100% sodium hydride used is then added. The resultant tertiary polyethyleneoxy -
50 n - alkylamine is quaternized by the following conventional procedure.

If a commercially available tertiary polyethleneoxy - n - alkylamine is used, it should be dried 2-4 hours at 90-95°C with agitation under reduced pressure
55 (30-50 mm of mercury; 3,999.7 to 6,666.1 pascal). To one mole of the aforesaid tertiary amine is slowly added, with agitation, 0.99-1.0 mole of dimethyl sulfate over a 1-4 hour period while the reaction mixture is kept at 50-60°C, after which the mixture is
60 agitated for an additional 8-20 hours at 50-60°C. When the reaction is complete, the product can either be used directly in the subsequent condensation step or stored until such use.

General procedure used to prepare
65 *agent of the invention*

The agent of the invention can be prepared by the following general procedure. Although the procedure given below applies to the preparation of an agent of the aforesaid formula having Y_1, Y_2 and Y_3
70 moieties, it will be obvious to one skilled in the art that other agents of said formula wherein one or both of Y_1 and Y_2 are absent can similarly be prepared.

A mixture of one mole of the lower alkyl
75 polyethyleneoxy alcohol (Y_1 precursor) and one mole of the higher alkyl polyethyleneoxy alcohol (Y_2 precursor) is dried and any peroxides therein are eliminated by heating, with agitation, at 170-190°C for 2 hours under reduced pressure (20-50 mm of
80 mercury; 2,666.4 to 6,666.1 pascal). After cooling to 80-90°C and breaking the vacuum with a nitrogen purge, one mole of the quaternized polyethyleneoxy tertiary amine glycol (Y_3 precursor), one mole of predried hexakis (methoxymethyl) melamine (X pre-
85 cursor) (Cymel® 300) and 0.6 weight%, based on the total weight of the components used, of predried p-toluenesulfonic acid are added. With rapid nitrogen purging of the molten mass, the stirred mixture is heated at 90-95°C. The methanol and small
90 amount of methylal that are evolved can be collected in cold receivers or traps. The total amount of methanol collected should be about three moles. The condensation is continued until the desired product viscosity is reached. An amount of tertiary
95 amine, preferably having a boiling point above 120°C, for example, triethanolamine, which is 50 mole% greater than the molar amount of p-toluenesulfonic acid used is added immediately to the viscous mass to stop the reaction. The nitrogen
100 flow rate and stirring rate are reduced while the amine neutralizes the acid at 85-95°C (10-20 minutes).

Aqueous dilution of condensate

The above 100% condensate can be stored as is or
105 used directly. However, for most uses, such as the treatment of textile fabrics, it is diluted (by suspending or dispersing or by dissolving in a normally liquid medium) to a manageable viscosity, for example, the desired application liquid viscosity, so
110 that it can be applied by conventional techniques, for example, by padding or exhaust. If the aforesaid 100% condensate has been stored at room temperature, it will be a solid and must be thawed at a temperature of at least 50°C, preferably under a nitrogen
115 atmosphere. The condensate can be diluted with a normally liquid (at 25°C) medium until the desired (manageable) viscosity is achieved. The liquid medium preferably should be miscible with the agent of the invention and the salt and/or polyacidic
120 compounds discussed hereinafter, nonreactive therewith at least up to about the cure temperature, and removable by volatilization at least by the cure temperature. Suitable liquid media include water, alcohols, ketones, esters, ethers and aromatic hyd-
125 rocarbons. A convenient liquid medium for textile treating operations is water. Most of the description herein relates to the use of water as the normally liquid medium in connection with the utility of the agent of the invention as a durable, antistatic, soil
130 release agent for textile fabrics. It will be readily

apparent to one skilled in the art that other subs-
trates can be treated with the agent of the invention
to achieve durable antistatic and soil release charac-
teristics. For example, the agent of the invention can
5 be used to treat textile fibers which may or may not
subsequently be converted to fabric and to treat
substrates which are flexible or nonflexible shaped
structures of polymeric materials other than textile
fibers and fabrics, for example, molded articles as
10 well as extruded products, such as film and tubing.
   If water is used as the normally liquid diluting
medium, a weighed portion of the viscous conden-
sate is added slowly to a rapidly stirred quantity of
water (the addition of water to the condensate may
15 yield a difficult - to - manage gel-like material). After
the condensate dissolves, the mixture is made
alkaline, for example, the pH is adjusted to 7.7-8.2, to
minimize hydrolysis of the product on storage, by
the addition of sodium bicarbonate. If desired,
20 enough water can be added to bring the mass to, for
example, a 20 weight% aqueous solution. Such a
solution has a Brookfield viscosity of 250 to 16,000
cps (0.250 to 16.000 pascal seconds) at 20°C. In the
treatment of fabrics, a more dilute aqueous solution
25 is used, for example, less than 1 weight% in an
exhaust application.
   The agent of the invention has a calculated
hydrophile-lipophile balance (HLB) of 14.5 to 18.0
and a 20 weight% aqueous solution viscosity, as
30 measured on a Brookfield viscometer, of 250 to
16,000 cps (0.250 to 16.000 pascal seconds). In gen-
eral, all other variables being maintained constant,
the higher the viscosity, the better will be the durabil-
ity achieved with the agent of the invention on the
35 fabric being treated.
   The Brookfield viscosity is determined by the
American Society of Testing Materials Test Method
D-1824, modified, with the modifications thereto
being as follows:
40   1. Viscosities are measured at 25 ± 0.4°C.
   2. Samples are bubble-free when viscosities are
determined.
   3. Viscosity is determined one to three times, on
a given sample, at about the same time.
45   4. Viscosities are reported in centipoises (cps;
pascal seconds).
   The hydrophile-lipophile balance (HLB) system is
the subject of numerous publications, for example,
"Classification of Surface-Active Agents by HLB," W.
50 C. Griffin, J. Soc. Cosmetic Chemists 1, 311 (1949);
"Calculation of HLB Values of Non-ionic Surfac-
tants," ibid. 5, 249 (1954); "The Atlas HLB System,"
Atlas Chemical Industries, Inc., Wilmington, Delaw-
are, 4th printing, May, 1971; Proceedings 2nd Int.
55 Congr. Sur. Act. 1, 426 (1957), Academic Press, New
York, N.Y. HLB values reflect the hydrophilic content
of the molecule. In accordance with the information
available from the aforesaid publications, calculated
HLB values are determined herein by means of the
60 equation:

$$\frac{\text{sum of the molecular weights of all the hydrophilic moieties of the molecule}}{\text{molecular weight of the entire molecule}} \cdot X\ 20 = \text{Calculated HLB}$$

65

The agent of this invention is particularly useful as
a textile treating agent for fabrics of synthetic fibers,
including woven, nonwoven and knit fabrics of
either spun or filamentary type fibers. The fabrics
70 can be of the blended or unblended fiber type. Fabr-
ics treated with the agent exhibit good to excellent
antistatic, soil release and, to some extent, anti-soil
redeposition characteristics. Moreover, the agent
does not substantially affect the hand of the fabric,
75 and the agent appears to be non-toxic, it can be
applied topically using pad or exhaust techniques, it
is durably retained by the fabric after being applied
thereto and it is resistant to yellowing on the fabric.
Fabrics particularly suitable to treatment with the
80 agent of this invention include those of polyester,
polyamide, polyacrylic or acetate fibers. Qiana®,
Nomex®, Dacron® and nylon taffeta fabrics, for
example, can be usefully treated by means of this
invention.
85   It is to be understood that the previous discussion
of preparative procedures of the agent of the inven-
tion and the following examples (within the inven-
tion) and experiments (outside the invention) are
intended merely as guidelines to enable one skilled
90 in the art to practice the invention. Modifications of
the preparative procedures disclosed herein will be
readily apparent. It is to be further understood that
the parameters set forth above for the agent of the
invention are important to achieving the objects of
95 the invention. Control of preparative conditions is
important to achieving the requisite parameters of
the agent and, although the details given above and
hereinafter in the examples are believed to be ade-
quate to practice the invention, ultimate determina-
100 tion of such practice usually is carried out by evaluat-
ing the agent, promptly after it is prepared, as to its
various characteristics according to the procedures
set forth below.
   The fabric used in the evaluation of the agent of
105 the invention is produced from commercially avail-
able Dacron® Polyester Fiber Type 56. The fabric is
white, undyed 150/34 (denier/gauge) double-knit
fabric. The fabric is scoured at 71°C for 20 minutes
with 0.5 gram/litre (0.001 m³) of Merpol® SH nonionic
110 detergent and 1 gram/litre (0.001 m³) of trisodium
polyphosphate. After being rinsed well with water
the fabric is dried.
   The agent to be evaluated is padded onto the
fabric so as to give an active ingredient level of 0.8
115 weight%, based on the weight of dry fabric. A typical
pad bath includes the necessary amount of active
ingredient, with the bath concentration being
adjusted for wet-pickup of the fabric, 0.75 weight%
of sodium sulfate, based on the total weight of the
120 bath, and sufficient citric acid to achieve a pH of 4.0.
Pad application can be carried out with a commer-
cially available padder, such as a Spartan® II padder,
using two passes and two nips. After padding, the
fabric is dried and cured at 199°C in a forced hot air
125 oven. Curing conditions may vary depending on the
wet pick-up of the fabric. Generally, 60 to 75 seconds
are adequate for curing at 199°C. A pin frame is used
to hold the fabric.
   The cured fabric is rinsed in Permutit® water to
130 remove residual salts or acids and then dried, for

example, in a commercially available Sears Roebuck
dryer, at 71 ± 5°C. The agent of the invention is
tested for its antistatic characteristic on the fabric
using the American Association of Textile Chemists
5 and Colorists (AATCC) Test Method 76-1975 with
slight modification as described below. Testing of
fabric samples is carried out in a dry box at 20 ± 2%
relative humidity and 23 ± 1°C, the humidity being
controlled by a commercially available Hygrometer
10 Indicator Controller (Model 15-3252) with a Model
15-1810 sensing element. Testing equipment
includes a Keithley Model 610C Electrometer in
combination with a Keithley Model 240A High Vol-
tage Supply and a Model 610S Resistivity Adapter.
15 Further description of this test may be found in the
AATCC Technical Manual under the aforesaid test
method which is entitled "Electrical Resistivity of
Fabrics." Testing of fabric samples is carried out ini-
tially (after rinsing) and then after five and ten home
20 laundering/tumble dry cycles, commonly referred to
as home wash/tumble dry (HWTD) cycles. The anti-
static (A.S.) data appear in the accompanying tables
under the heading "A.S.," with the symbols "I, 5W,
10W" being used to indicate the antistatic charac-
25 teristic initially and after five and ten washes (HWTD
cycles), respectively. As indicated above, the agent
of the invention must exhibit an electrical resistivity
(Keithley Log R), a measure of the antistatic charac-
teristic of the agent, on polyester fabric, at 20 ± 2%
30 relative humidity and 23 ± 1°C, of no greater than
13.00 initially and no greater than 14.25 after ten
washes. For comparison, it may be noted that clean,
untreated cotton broadcloth at about 20% relative
humidity and about 23°C exhibits a Keithley Log R of
35 13.65 ± 0.05. Untreated synthetic fabrics, in general,
exhibit Keithley Log R values of 15.5 to 16.0.
   The home launderings are carried out, in general,
according to AATCC Test Method 124. Equipment
used includes a Sears Roebuck Kenmore automatic
40 washer (Model 600) and a Sears Roebuck Kenmore
automatic dryer (Model 600). This is the same dryer
described above for drying the fabric samples which
have been rinsed in Permutit® water. Test fabric
specimens are cut to 20.3 cm squares and intro-
45 duced into the washer along with "load fabric"
(hemmed pieces of cotton sheeting; 97.4 cm
squares) to give a total dry load of 1.81 kilograms. To
the washer are added 28 grams of Tide® (commer-
cially available) detergent. Washing is carried out
50 under a normal wash cycle (12 minutes), at the high
water level setting, using a hot water temperature of
60 ± 3°C. The temperature of the rinse water used is
41 ± 3°C. Soft water (hardness of no more than 5
ppm) is used. For hard water, Calgon® is added in an
55 amount sufficient to reduce the hardness to a max-
imum of 5 ppm. Following washing and spin-drying
the fabrics are dried in the dryer at a normal cycle
time of 45 minutes, with the temperature dial being
set on high to give a maximum stack temperature of
60 71 ± 9°C. This cycle is repeated to achieve the
desired number of home launderings.
   The soil release (S.R.) characteristic of the agent of
this invention is determined, in general, by AATCC
Test Method 130. The treated and cured fabric sam-
65 ples used in the soil release test are prepared in the

same manner as those used in the antistatic perfor-
mance test described above. The soil release test
measures the ability of a fabric to release oily stains
during home laundering and, as indicated above, the
70 agent of this invention must exhibit a soil release
rating on polyester fabric of at least 3 (initial), that is,
before being subjected to the home laundering test.
Data relative to this test are provided in the accom-
panying tables under the heading "S.R.", with data
75 being included to show the soil release ratings ini-
tially (I) and after five (5W) and ten (10W) washes
(HWTD cycles). Test specimens measuring 10 cm x
20 cm are conditioned for four hours at 21 ± 1°C and
65 ± 2% relative humidity prior to staining. A single
80 flat thickness of test specimen is placed on AATCC
Textile Blotting Paper on a smooth horizontal sur-
face and five drops (each having a volume of about
0.2 ml; 0.2×10^{-6} m^3) of a commercially available oil
test liquid (60 weight% Nujol® and 40 weight% used
85 piston engine automotive oil) are applied to the test
specimen. The oil puddle (total volume, about 1 ml;
1×10^{-6} m^3) which is formed is covered by a 7.6 cm x
7.6 cm piece of glassine paper and a 2.28 kilogram
weight is placed on the paper. After 60 seconds the
90 weight is removed and the glassine sheet is dis-
carded. The oil-stained fabric specimen is then sub-
jected to washing. Washing is carried out within 15
to 60 minutes of staining with such a number of test
specimens that the total number of oil stains in the
95 wash does not exceed thirty. Setting a maximum
limit on the number of oil stains provides latitude in
selecting the number of test specimens used in the
event that it is desirable to place more than one oil
stain on each test specimen. The aforesaid Kenmore
100 Model 600 automatic washer is filled to the high
water level with water at a temperature of 60 ± 3°C.
To the washer are added 140 ± 5 grams of AATCC
Standard Detergent 124, or a known equivalent.
Then the test specimens and cotton sheeting ballast,
105 so as to make a total load of 1.8 ± 0.1 kilograms, are
introduced. The washer is run through a normal
wash cycle (12 minutes). Following completion of
the spin-dry cycle, the specimens and ballast are
placed in the aforesaid Kenmore Model 600 dryer.
110 Drying is carried out at the high setting (70 ± 6°C),
maximum stack temperature, for 45 ± 5 minutes.
The dried test specimens are rated for residual stains
within four hours after drying. Evaluation is made by
comparing the residual stains in the test specimen
115 with a standard soil release rating chart. Stains are
rated to the nearest whole number from 1 to 5. The
higher the number, the less is the residual stain.
   As stated above in the formula definition of the
agent of this invention, R_3 preferably is C_{8-18} alkyl or,
120 to achieve good water wettability (drop absorption),
R_3 preferably is C_{8-12} alkyl. The drop absorption test
used herein is, in general, based on AATCC Test
Method 39. This test employs the same type of tre-
ated/cured fabric specimens described above. Fabric
125 specimens are conditioned at 65 ± 2% relative
humidity and 21 ± 1°C for at least four hours before
testing. Each fabric test specimen is placed over the
mouth of the cap of a 5.1-7.6 cm diameter jar. Water
is dropped onto the surface of the fabric in a drop-
130 wise fashion from a conventional eye dropper (each

drop having a volume of about 0.2 ml; 0.2×10^{-6} m³)
held about 1 cm above the surface of the fabric. The
time is measured, using a stop watch, from the
moment that the first drop falls from the dropper
5 until the wet area of the fabric loses its specular
reflective power. This can best be observed by plac-
ing the fabric between the observer and a source of
light, such as an outside window, at such an angle
that the specular reflection of light from the surface
10 of the flattened drop (as the drop hits the surface)
can be plainly seen. As the drop is absorbed by the
fabric, specular reflection of light ceases and a dull
wet spot is formed on the fabric. High drop absorp-
tion times, for example, above 5 seconds, indicate
15 poor wettability of the treated fabric.

Additional information on all of the aforesaid test
procedures may be found in the AATCC Technical
Manual.

Although the aforesaid testing procedures involve
20 application of the agent of the invention to polyester
fabric, optimum benefits from the agent of the inven-
tion are achieved using specialized techniques of
application that are tailored to the type and charac-
teristics of the fabric being treated. Details of these
25 techniques are discussed below.

The application procedure for the agent of the
invention is similar to procedures known in the trade
for applying textile treating agents or fabric con-
ditioners of the type disclosed herein. For example,
30 procedures employed in the application of commer-
cially available Zelcon® TGF Fabric Conditioner to
polyester and certain polyester blend fabrics are
similar to the procedure required to apply the agent
of this invention to fabric materials. The results
35 achieved with the agent of the invention are readily
distinguishable from the results achieved with prior
art textile treating agents such as Zelcon® TGF Fabric
Conditioner. For example, whereas fabric treated
with the latter, using conventional application condi-
40 tions, does not exhibit durable (to home washes)
antistatic behavior, fabric treated with the agent of
the invention, using the application procedure
described herein, retains its antistatic behavior
through numerous home washes (HWTD cycles).
45 This durability characteristic of the agent of the
invention is believed to be related to the water -
insolubilization which takes place during curing of
the agent on the fabric.

As already indicated above, the agent of this
50 invention can be applied by pad or exhaust proce-
dures. In either procedure, the dilute aqueous con-
densate described hereinabove, for example, the 20
weight% aqueous solution, must include certain
acids and/or salts before it is applied to the fabric
55 which is to be treated. The addition of an organic
polyacidic compound and/or an at least divalent
inorganic acid provides antistatic durability of the
agent of the invention, when padded onto the fabric,
through at least ten washes. The addition of a salt of
60 a mono-, di- or trivalent metal or of an ammonium
cation provides both soil release and antistatic dura-
bility of the agent, when either padded or exhausted
onto the fabric, through at least ten washes. Prefer-
ably, for pad application, both the acid and the salt
65 are present along with the agent of the invention to

achieve maximum effects. It has been found that, in
exhaust application, the salt must be used alone. In
other words, exhaust application cannot be carried
out with acid along or with the combination of acid
70 and salt. Regarding the polyacidic organic com-
pound and the at least divalent inorganic acid, the
second dissociation constant thereof must be grea-
ter than 1×10^{-8}. Examples of such materials include
citric, oxalic, tartaric, succinic, glutaric and phos-
75 phoric acids. Boric acid, on the other hand, is
unsatisfactory because the second dissociation con-
stant is below the aforesaid minimum value. It has
been found that low molecular weight polyacrylic
acids also are useful herein. Although such materials
80 are polyacidic, the various dissociation constants of
the carboxy groups are not readily determinable
because of the polymeric nature of the material. The
operability of such an acid herein suggests that it
meets the aforesaid requirement on second dissoci-
85 ation constant. Useful polyacrylic acids include
those which are readily soluble in water. Such mater-
ials include those having molecular weights up to at
least 5,000. In using the polyacidic compound, alone
or in combination with the salt, the pH of the treating
90 bath should be in the range 3.0 to 6.0, preferably 4.0
to 5.5. The function of the salt of a mono-, di- or
trivalent metal or an ammonium salt, including an
appropriate quaternary ammonium salt, appears to
be related to its ability to lower the cloud point of the
95 dilute aqueous solution of the agent of the invention
below 100°C. The salt should have sufficient ionic
strength to lower the cloud point below 100°C but it
should not be such as to insolubilize the product at
ambient temperature (25°C). Lowering of cloud point
100 is determined using a 0.2 weight% aqueous solution
of the agent. Examples of salts which may be emp-
loyed herein alone or in combination with the
organic polyacid include, but are not limited to, cal-
cium, magnesium, zinc and sodium nitrates, the
105 sodium phosphates, such as disodium hydrogen
phosphate and trisodium phosphate, sodium, mag-
nesium and calcium chlorides, sodium, magnesium,
zinc and aluminum sulfates, sodium and ammonium
oxalates, calcium acetate and diammonium citrate.
110 Salt hydrates are equally useful. The use of the salt
permits selective deposition of the agent of the
invention during padding or exhaust; it decreases
the mobility of the agent of the invention during the
cure cycle and, thus, the agent is retained through-
115 out the fabric (i.e., substantial amounts do not
migrate); and it enhances the crosslinking which
takes place during the drying/curing step as water is
evaporated from the treated fabric. In general, it may
be said that the cloud point is raised as the HLB
120 increases but is lowered as the Brookfield viscosity is
increased.

To exhaust the agent of the invention onto the
fabric, the exhaust bath containing the agent, the
appropriate salt, in an appropriate amount, and
125 fabric material is heated to within about 5 to 10°C, for
example, about 6°C, of the cloud point and held there
until exhaust is complete. This is usually effected in
no more than 5 to 10 minutes, for example, 6
minutes. The treated fabric is then removed from the
130 exhaust bath, rinses or not rinsed (not rinsing is pre-

ferred). cooled, extracted of water (using conventional exhaustion techniques to remove excess water) and cured. Curing conditions will vary depending on the moisture content of the fabric, the
5 higher the moisture content, the longer the time and/or the higher the temperature required. In general, for exhaust and pad applications, curing is carried out at 149 to 204°C. A preferred temperature range is 193 to 199°C. Curing at the preferred temp-
10 erature conveniently can be carried out in less than one minute, for example, in 15 to 30 seconds, depending on moisture content and the weight of the fabric, when the agent of the invention is applied by exhaust techniques. For padding operations wherein
15 moisture levels are higher, longer times usually are required, for examples, 60 to 75 seconds. Durability of the agent of the invention on the fabric requires careful control of curing conditions. Under-curing as well as over-curing will result in diminished durability of
20 the agent. It is to be understood that curing conditions must be determined, for the most part, empiri-

cally. For example, a hydrophilic fabric (that is, one retaining moisture readily) will require more rigorous curing conditions than a hydrophobic fabric.
25 Similarly, selection of salt and/or acid, and the amount thereof, are usually determined empirically. Evidence of the criticality of the curing conditions, in general, is provided in Table I. The table shows the antistatic and soil release behavior of the agent of
30 the invention on the fabric initially and after five and ten washes. The agent used was that of Example 26 and the fabric to which the agent was applied was the same at that described above for test evaluation of the agent of the invention. The agent was applied
35 to the fabric by padding from a pad bath (of such concentration as to give 0.8 weight % of the agent on the fabric, dry weight) containing 0.75 weight % of sodium sulfate, based on the total weight of the bath, and citric acid to a pH of 4.0. Conditions of
40 drying/curing of the treated fabric are given in the table. As noted, in some instances, curing was preceded by a short drying step at a lower temperature.

TABLE I
Cure Conditions

Time (min)	Temp. (°C)	A.S.			S.R.		
		I	5W	10W	I	5W	10W
3	149	11.62	13.25	13.25	3	3	—
3	163	11.84	13.47	13.25	3	3	—
2	177	11.56	12.91	13.35	3	3	—
2	191	12.43	14.13	14.61	3	3	—
6	149	11.81	13.39	14.17	3	3	—
6	163	12.50	14.73	15.08	3	2	—
6	177	12.59	15.25	15.18	2	1	—
4	177	12.70	15.69	16.03	3	2	—
1	191	11.95	14.35	15.91	3	1	—
1	193	11.69	12.88	13.25	4	3	1
1	199	11.69	13.08	13.25	3	3	1
1	204	11.62	12.83	13.07	3	3	1
1	204	11.85	13.96	14.73	2	1	—
1.5	204	11.65	13.13	13.41	3	3	—
0.75	204	12.10	14.69	16.73	2	1	—
0.75	193	12.63	15.56	15.39	4	1	—
1	193	11.56	13.50	13.65	4	1	—
1.25	193	11.59	13.08	13.39	4	4	—
1.5	193	11.62	13.19	13.47	4	3	—
0.25*	193	11.24	12.81	13.08	3	4	—
0.5*	193	11.65	13.07	13.18	3	3	—
0.5*	193	12.43	13.37	13.56	3	3	—
0.75*	193	14.50	14.43	14.61	4	1	—
1*	193	13.24	14.95	15.53	4	3	—

*dried 3 minutes at 121°C.

Table II which follows includes data showing the effect of the addition of a salt and/or an acid to the
45 agent of the invention in connection with the use of the agent in the pad (except as noted) treatment of fabric of the same type as that described above for test evaluation of the agent of the invention. The methods used to apply the agent were substantially
50 the same as those described above. The first column in Table II refers to the examples (hereinafter) in which the agent was made. Weight % concentrations shown are based on the total weight of the pad or exhaust bath.

TABLE II

	Agent from Ex. No.	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
5	3	Diammonium citrate	0.1	—	—
	3	"	0.2	—	—
10	3	Diammonium citrate/ Sodium sulfate	0.1/ 0.75	—	
	3	"	0.2/ 0.75	—	—
15	8	—	—	Polyacrylic M.W. 2,000	(0.3%)
	8	—	—	Polyacrylic M.W. 5,000	(0.4%)
20	15	Calcium chloride	0.6	—	—
	15	Calcium chloride	0.4	Citric	4.0
	15	Sodium nitrate	0.3	Polyacrylic M.W. 5,000	5.5
25	17	Calcium acetate	0.6	Citric	4.0
	17	"	"	"	"
	17	"	0.93	"	"
	17	"	"	"	"
30	17	Calcium nitrate	0.75	"	"
	17	"	1.25	"	"
	24	Sodium nitrate	0.45	Citric	4.0
35	24	Zinc sulfate	1.0	"	"
	24	Zinc nitrate	1.0	"	"
	24	Magnesium sulfate	0.5	"	"
40	24	Magnesium nitrate	0.8	"	"
	26	—	—	—	—

TABLE II (Cont'd.)

Agent From Ex. No.	Dry/Cure Temp. (°C)	Time (min.)	I	A.S. 5W	10W	I	S.R. 5W	10W
3	193	1.0	13.06	14.61	15.20	4	2	1
3	"	"	12.13	13.33	13.23	4	3	2
3	"	"	13.02	14.43	14.65	4	5	2
3	"	"	11.97	13.39	13.47	4	4	3
8	"	0.5	11.75	13.59	14.13	4	3	3
8	"	"	11.65	13.43	13.61	4	4	3
15	199	"	11.88	13.65	14.25	4	2	2
15	193	1.0	11.84	13.47	13.95	5	4	2
15	"	"	11.65	13.03	13.11	5	5	3
17	"	"	11.96	13.84	13.20	4	4	1
17	"	"	11.69	13.19	13.23	4	4	2
17	"	"	12.15	14.18	13.96	4	4	1
17	"	"	11.56	13.04	14.01	4	5	2
17	"	"	12.37	13.56	13.17	4	5	5
17	"	"	12.63	13.96	13.18	4	5	3
24	"	"	11.93	13.00	13.61	3	5	5
24	"	"	12.31	14.11	14.18	3	4	5
24	"	"	13.25	14.39	14.07	3	3	2
24	"	"	12.11	13.39	13.73	3	5	5
24	"	"	12.23	13.41	13.47	3	3	5
26	—	—	12.56	14.69	—	3	1	—

TABLE II (cont'd)

Agent from Ex. No.	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
26*	Sodium sulfate	0.75	—	—
26	"	"	Tartaric	4.0
26	"	"	Citric	5.5
26	"	"	Glutaric	4.0
26	"	"	Succinic	4.0
26*	Calcium nitrate	"	—	—
26*	$Na_2HPO_4 \cdot 7H_2O$	1.0	—	—
26	"	0.75	Tartaric	4.0
26	"	"	Citric	5.5
26*	$Na_3PO_4 \cdot 12H_2O$	1.25	—	—
26*	Magnesium chloride $\cdot 6H_2O$	0.5	—	—
26**	Sodium chloride	"	—	—
26**	Sodium nitrate	"	—	—
26	Aluminum sulfate	"	—	—
26**	Sodium oxalate	0.4	—	—
26	"	0.25	Oxalic	5.0
26	"	"	Citric	5.5
26	—	—	Succinic	4.0
26	—	—	Tartaric	4.0
26	—	—	"	4.5
26	—	—	"	5.0
26	—	—	"	5.5
26	—	—	"	6.0
26	—	—	Citric	4.0
26	—	—	"	4.5
26	—	—	"	5.0
26	—	—	"	5.5

TABLE II (Cont'd.)

Agent from Ex. No.	Dry/Cure Temp. (°C)	Time (min)	A.S. I	5W	10W	S.R. I	5W	10W
26*	199	0.5	12.12	12.87	13.43	5	3	2
26	"	1.0	11.65	12.94	13.56	4	4	4
26	"	"	12.73	12.73	13.59	4	3	3
26	"	1.25	12.13	13.53	13.59	—	—	—
26	"	"	12.12	13.61	15.01	—	—	—
26*	"	0.5	12.09	13.01	13.41	4	3	4
26*	"	"	11.96	13.03	13.61	5	3	4
26	"	1.0	12.27	13.25	14.24	3	4	3
26	"	"	11.23	12.73	13.43	3	3	4
26*	193	0.5	12.06	13.13	13.35	4	3	2
26*	"	"	12.33	13.33	13.73	3	3	3
26**	"	"	12.56	13.33	14.04	4	3	3
26**	"	"	12.37	13.59	14.13	4	3	—
26	199	1.25	12.14	13.65	13.95	3	3	2
26*	"	0.5	12.04	13.00	13.61	5	4	5
26	"	1.25	11.93	13.45	13.86	3	2	2
26	"	"	11.59	13.39	13.21	4	—	—
26	"	"	12.19	13.87	13.73	—	1	—
26	"	1.0	11.65	12.85	13.39	3	1	—
26	"	"	11.83	13.00	13.61	3	1	—
26	"	"	12.17	13.33	14.05	3	1	—
26	"	"	11.84	13.59	14.50	3	1	—
26	"	"	12.21	14.08	14.73	2	1	—
26	"	"	12.81	14.25	15.23	3	1	—
26	"	"	11.96	13.18	13.96	3	1	—
26	"	"	11.97	13.53	14.21	3	1	—
26	"	"	11.69	13.24	13.73			

TABLE II (Cont'd.)

Agent from Ex. No.	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
26	—	—	Citric	6.0
26	—	—	Oxalic	4.0
26	—	—	"	4.5
26	—	—	"	5.0
26	—	—	"	5.5
26	—	—	"	6.0
26	—	—	Boric	(0.05%)
26	—	—	"	(0.1%)
26	—	—	"	(0.2%)
26	—	—	"	(0.4%)
26	—	—	"	(0.6%)
26	—	—	85% H_3PO_4	4.0
26	—	—	"	4.5
26	—	—	"	5.0
27	—	—	—	—
27	Calcium nitrate	0.75	—	—
28	—	—	—	—

TABLE II (Cont'd.)

Agent From Ex. No.	Dry/Cure Temp. (°C)	Time (min)		A.S.			S.R.	
			I	5W	10W	I	5W	10W
26	199	1.0	11.96	13.65	14.47	3	2	1
26	"	"	11.84	13.10	13.56	3	2+	—
26	"	"	12.01	13.13	13.69	3	2	—
26	"	"	11.56	12.84	13.35	3	1	—
26	"	"	12.05	11.93	14.43	3	1	—
26	"	"	11.98	13.96	14.47	3	1	—
26	"	"	12.19	14.21	15.07	3	1	—
26	"	"	12.25	14.61	14.98	3	1	—
26	"	"	11.88	13.35	13.96	4	1	—
26	"	"	13.11	14.59	15.73	3	1	—
26	"	"	13.21	15.21	15.95	3	1	—
26	"	1.25	11.85	13.13	13.93	4	4	—
26	"	"	12.19	13.33	14.25	4	4	—
26	"	"	12.11	13.22	13.90	4	4	—
27	193	1.0	12.87	15.04	15.56	3–4	1	1
27	199	"	11.73	13.99	13.45	4	3	3
28	193	"	13.13	14.69	15.47	3	1	1

*Applied to fabric by exhaust: 10 minutes at 66°C.
**Applied to fabric by exhaust: 10 minutes at 49°C.

Table III which follows includes data showing the effect of the addition of a salt and/or an acid to the agent of the invention in connection with the use of the agent in the treatment of fabrics other than that specified above in connection with the data included in Table II. In all cases, the agent of the invention used was that of Example 26. Thus, the headings of Tables II and III are the same except that in the latter the Example No. heading has been replaced by the heading to designate the type of substrate fabric. Application of the agent was carried out by padding as already described above.

TABLE III

	Fabric	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
5	Woven Qiana®	calcium nitrate	0.25	Citric	4.0
	"	"	0.75	"	"
	"	sodium sulfate	0.25	"	"
10	"	"	0.75	"	"
	"	$Na_2HPO_4 \cdot 7H_2O$	1.0	"	"
	"	"	0.5	"	"
	Knit Qiana®	sodium sulfate	0.75	—	—
15	"	"	0.75	Citric	4.0
	"	—	—	"	"
	White Qiana®	sodium sulfate	0.75	"	"
	"	"	"	"	"
20	"	"	"	"	"
	Nomex®	—	—	Oxalic	"
	"	sodium sulfate	0.5	Tartaric	"
	"	"	"	Citric	"
25	Red Nylon Taffeta	calcium nitrate	0.75	"	"
	"	"	0.25	"	"
	"	sodium sulfate	0.75	"	"
30	"	"	0.25	"	"
	"	$Na_2HPO_4 \cdot H_2O$	1.0	"	"
	"	"	0.25	"	"
	Dull Spun Acetate Suiting	"	0.5	"	"
35	"	"	"	Tartaric	"
	"	—	—	Citric	"
	Acetate	sodium sulfate	0.5	"	"
40	"	$Na_2HPO_4 \cdot 7H_2O$	"	"	"

TABLE III (Cont'd.)

	Fabric	Dry/Cure Temp. (°C)	Time (min)	I	A.S. 5W	10W	I	S.R. 5W	10W
5	Woven Qiana®	193	0.75	11.5	12.66	13.43	3	4	3
	"	"	"	11.89	13.03	14.19	3	3	3
	"	"	"	11.94	13.08	14.10	3	3	2
10	"	"	"	11.79	12.70	13.73	3	3	3
	"	"	"	12.25	13.50	14.65	3	3	2
	"	"	"	12.14	13.25	14.39	3	3	2
	Knit Qiana®	"	"	11.73	12.63	13.25	5	5	3
15	"	"	"	11.69	13.13	13.25	4	5	5
	"	"	"	12.08	12.90	13.47	3	5	4
	White Qiana®	182	1.0	12.08	13.53	14.19	5	3	3
20	"	193	0.5	11.87	13.99	14.73	5	3	2
	"	"	0.75	12.06	15.04	14.19	5	4	3
	Nomex®	188	1.0	13.28	13.88	14.25	3	3	—
	"	"	"	13.07	13.43	13.73	3	4	—
	"	"	"	13.02	13.73	14.32	3	3	—
	Red Nylon Taffeta	193	0.5	11.53	12.35	12.95	5	5	—
25	"	"	"	11.65	12.73	13.45	5	5	—
	"	"	"	12.03	12.96	13.65	5	5	—
	"	"	"	12.13	13.09	13.65	5	5	—
	"	"	"	12.09	13.45	14.24	5	5	—
30	"	"	"	12.07	13.15	13.23	5	5	—
	Dull Spun Acetate Suiting	182	0.75	12.73	13.25	13.73	2	2	—
	"	"	"	12.94	13.31	13.96	2	2	—
35	"	"	"	13.22	13.65	14.00	2	2	—
	Acetate	199	"	12.39	13.41	14.73	3	5	—
	"	182	"	12.45	13.53	14.25	2	5	—

TABLE III (Cont'd.)

	Fabric	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
40			"		"
45	Acrilan® Type 16 Plain Weave	Sodium sulfate	"	"	"
	"	Na₂HPO₄ · 7H₂O	"	"	"
	"	—	—	Tartaric Citric	"
50	Orlon® Type 75 Spun Yarn Plain Weave	Na₂HPO₄ · 7H₂O	0.5		
	"	—	—	Tartaric Citric	5.0 / 4.0
55	Arnel® Filament Tricot	Na₂HPO₄ · 7H₂O	0.5	Tartaric Citric	" / 5.0
	"	"	"	"	4.0
60	Spun Arnel® Plain Weave	Na₂HPO₄ · 7H₂O	0.5	Tartaric	"
	"	sodium sulfate	"	"	"
	"	Na₂HPO₄ · 7H₂O	"	"	"
65	"	—	—		

TABLE III (Cont'd.)

|	Fabric	Dry/Cure Temp. (°C)	Time (min)	I	A.S. 5W	10W	I	S.R. 5W	10W
5	Acrilan® Type 16 Plain Weave	182	0.75	11.87	12.27	13.24	3	2+	—
	"	"	"	12.25	13.00	13.88	3	2+	—
	"	"	"	11.97	12.63	13.61	3	3–	—
10	Orlon® Type 75 Spun Yarn Plain Weave	"	"	12.31	13.50	14.25	3	2	—
	"	"	"	12.56	14.05	14.35	2	2	—
15	Arnel® Filament Tricot	"	"	12.70	13.59	—	3	3	—
	"	"	"	12.73	13.84	—	3	3	—
	"	"	"	13.10	14.25	—	3	3	—
20	Spun Arnel® Plain Weave	"	"	12.01	13.25	13.61	2	2	—
	"	"	"	12.13	13.06	13.56	2	2	—
	"	"	"	11.98	12.70	13.50	2	2	—
25	"	"	"	12.17	13.35	13.98	2	2	—

The amount of agent of the invention applied to the substrate being treated therewith will vary with the substrate and the nature and extent of the effect

30 desired. For most textile applications, however, it has been found that 0.4 to 2.0 weight % of the agent on the fabric, based on the weight of dry fabric, imparts excellent, durable, antistatic soil release characteristics to the fabric. Generally, the preferred

35 amount is 0.8 ± 0.1 weight %.

It also has been discovered in connection with this invention that the process of application of the agent of the invention to the substrate, as described herein, need not be followed in its entirety with

40 respect to the treatment of certain substrates. More particularly, if the substrate is of sufficient polyacidic nature, the polyacidic compound described above need not, of necessity, be present in the treating bath. For example, fabrics made of fibers of acid-

45 modified polymers, such as the commercially available acid-modified polyamides and acid-modified polyesters, can be usefully treated with the agent of the invention in the absence of the aforesaid requisite salt and/or polyacidic compound, that is, using

50 only conventional aqueous treating bath ingredients, if sufficient acid-function is provided by the acid-modified polymer.

Examples 1 to 45

The following Examples 1 to 45 are intended to

55 show various embodiments of the agent of the invention and the characteristics thereof. The techniques used in the examples to prepare the agents and to apply them to polyester fabric for evaluation are substantially the same as those already

60 described above. More specifically with regard to the application of the agent to fabric, the agent included 0.75 weight %, based on the weight of bath, of sodium sulfate and sufficient citric acid to achieve a pH of 4.0. Dry/cure was affected in 1.0 to 1.25

65 minutes at 193 to 199°C. Data summarizing Exam-

ples 1 to 45 are given in Table IV. All of the embodiments of the examples, except as noted below, are of the formula

70

75

$$(Y_1)_a$$
$$X — (Y_3)_c$$
$$(Y_2)_b$$

wherein X is

and
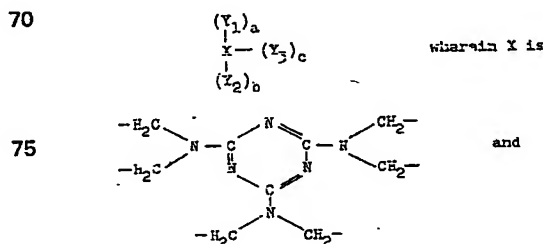
80

Y_1, Y_2, Y_3, a, b and c are as shown in the table. The various code designations shown in the table for Y_1, Y_2 and Y_3 are defined as follows:

85 A_1: $O(C_2H_4O)_{12}CH_3$
A_2: $O(C_2H_4O)_{16}$ straight chain $C_{13}H_{27}$
A_2': $O(C_2H_4O)_{15}$ branched chain $C_{13}H_{27}$
B_2: $O(C_2H_4O)_5$ straight chain $C_{13}H_{27}$

90 B_2': $O(C_2H_4O)_5$ branched chain $C_{13}H_{27}$
C_2: $O(C_2H_4O)_{25}$ straight chain $C_{13}H_{27}$
C_2': $O(C_2H_4O)_{25}$ branched chain $C_{13}H_{27}$
D_2: $O(C_2H_4O)_8$ straight chain $C_{13}H_{27}$
D_2': $O(C_2H_4O)_8$ branched chain $C_{13}H_{27}$

95 E_2: $O(C_2H_4O)_{45}$ straight chain $C_{13}H_{27}$
F_2: $O(C_2H_4O)_{88}$ straight chain $C_{13}H_{27}$

A_3 to M_3: $[(OC_2H_4)_m — N^{\oplus}R_3 — (C_2H_4O)_n H \quad A^{\ominus}]$
                                        R_4

100
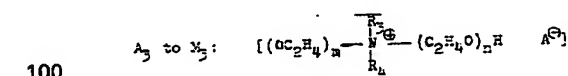
wherein $A^{\ominus}$ is $^{\ominus}OSO_3CH_3$ and for A_3 to M_3 the following apply:

	R_3	R_4	$m + n$
A_3:	$C_{18}H_{37}$	CH_3	50
B_3:	$C_{18}H_{37}$	CH_3	16
C_3:	C_8H_{37}	CH_3	50
D_3:	$C_{18}H_{35}$	CH_3	24
E_3:	C_8H_{17}	CH_3	16
F_3:	$C_{12}H_{25}$	CH_3	42
G_3:	C_4H_9	CH_3	50
H_3:	benzyl	CH_3	50
I_3:	C_8H_{17}	CH_3	24
J_3:	C_4H_9	C_4H_9	50
K_3:	C_4H_9	CH_3	12
L_3:	$C_{12}H_{25}$	CH_3	30
M_3:	C_8H_{17}	CH_3	100

In Example 44, X is
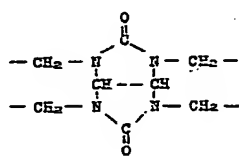
TABLE IV

Ex. No.	(a)	Y_1	(b)	Y_2	(c)	Y_3	HLB	Viscosity (pascal seconds)
1	0	—	0	—	1	A_3	15.4	1.300
2	1	A_1	0	—	1	A_3	16.1	1.300
3	2	A_1	0	—	1	A_3	16.6	0.560
4	0	—	2.3	A_2	1	A_3	15.6	8.280
5	0	—	2	A_2	1	A_3	15.6	0.580
6	0	—	2	B_2	1	A_3	14.5	8.200
7	0	—	1	C_2	2	A_3	16.7	2.000
8	1	A_1	1.2	A_2	1	A_3	16.1	0.610
9	1	A_1	1	A_2	1	A_3	16.1	4.600
10	1	A_1	1	A_2	1	A_3	16.1	7.680
11	1	A_1	1	A_2'	1	A_3	16.1	1.440
12	1	A_1	1	D_2	1	A_3	15.8	3.200
13	1	A_1	1	B_2'	1	A_3	15.6	0.824
14	1	A_1	1	D_2'	1	A_3	15.8	2.720
15	1	A_1	1	C_2	1	A_3	16.4	8.780
16	1	A_1	1	E_2	1	A_3	17.0	6.180
17	0.8	A_1	1.2	A_2	1	A_3	16.0	7.300
18	0.5	A_1	1.5	A_2	1	A_3	15.8	5.900
19	0.8	A_1	1.2	C_2	1	A_3	16.4	10.800
20	0.8	A_1	1.2	C_2	1	A_3	16.4	5.740
21	0.5	A_1	1.5	C_2	1	A_3	16.4	11.760
22	0.5	A_1	1.5	C_2	1	A_3	16.4	4.120
23	1	A_1	1	C_2	1	A_3	16.5	6.060
24	1	A_1	1	C_2	1	A_3	16.5	8.800
25	1	A_1	1	C_2	1	A_3	16.5	8.960
26	1	A_1	1	C_2	1	A_3	16.5	8.200
27	1	A_1	1	C_2	1	A_3	16.5	2.400
28	1	A_1	1	C_2	1	A_3	16.5	2.400
29	1	A_1	1	C_2	1	B_3	14.9	4.450
30	1	A_1	1	C_2	1	C_3	17.1	1.820
31	1	A_1	1	C_2	1	C_3	17.1	8.050
32	1	A_1	1	C_2	1	D_3	15.5	7.600

TABLE IV (Cont'd.)

Ex. No.	I	A.S. 5W	10W	I	S.R. 5W	10W
1	11.96	12.07	12.95	3	3	2
2	11.89	—	12.99	4	3	3
3	11.98	14.25	13.47	4	4–5	5
4	11.65	13.33	14.03	4	4	4
5	12.59	13.85	14.13	4	4	3
6	11.69	13.30	13.53	4	3	2
7	11.73	13.18	13.73	4	4	3
8	11.59	13.19	13.08	4	5	3
9	11.78	13.03	13.41	4	3	3
10	11.73	13.08	13.59	3	2	2
11	11.77	12.99	13.98	4	4	3
12	11.79	14.11	—	4	3	—
13	11.62	12.90	13.61	4	3	2
14	11.91	13.03	13.43	4	4	3
15	11.69	12.95	13.43	4	4	3
16	12.17	13.37	13.56	4	4	3
17	11.79	13.43	13.13	4	4	2
18	11.73	13.19	13.22	4	4	3
19	11.94	12.88	13.13	5	4	3
20	12.04	13.13	13.47	4	4	3+
21	11.45	13.13	13.53	4	2	3
22	11.97	13.18	13.25	3	4	3
23	11.73	13.41	13.95	4	4	3
24	11.84	13.14	13.43	3	4	3
25	12.03	13.25	13.73	4	4	3
26	11.47	12.92	13.45	3	2	—
27	11.41	12.73	13.61	3	3	2
28	11.62	12.83	13.07	3	3	1
29	12.28	13.20	13.49	3	2	2
30	11.81	12.53	13.04	4	4	2
31	11.50	12.39	12.88	4	2	1
32	11.62	13.19	12.95	4	4	3

TABLE IV (Cont'd.)

Ex. No.	(a)	Y_1	(b)	Y_2	(c)	Y_3	HLB	Viscosity (pascal seconds)
33	1	A_1	1	C_2	1	E_3	15.7	1.800
34	1	A_1	1	C_2	1	F_3	16.7	0.950
35	1	A_1	1	C_2	1	F_3	16.7	2.700
36	1	A_1	1	C_2	1	G_3	17.3	2.712
37	1	A_1	1	C_2	1	H_3	17.2	2.770
38	1	A_1	1	C_2	1	I_3	16.2	12.700
39	1	A_1	1	C_2	1	J_3	17.2	6.200
40	1	A_1	1	C_2	1	K_3	15.8	1.000
41	1	A_1	1	C_2	1	L_3	16.3	2.750
42	1	A_1	1	B_2	1	A_3	15.6	0.420
43	1	A_1	1	F_2	1	A_3	17.8	2.860
44	1	A_1	1	C_2	1	A_3	16.8	4.200
45	1	A_1	1	C_2'	1	A_3	16.5	4.360

	A.S.				S.R.	
Ex. No.	I	5W	10W	I	5W	10W
33	11.95	13.11	13.98	5	4	4
34	11.30	12.59	12.73	3	1	1
35	11.29	12.59	12.70	3	2	1
36	12.14	13.02	14.20	4	4	2
37	11.86	13.53	13.69	3	2	2
38	12.14	12.70	13.39	4	3	2
39	11.65	13.07	14.03	3	1	—
40	11.56	14.02	—	4	1	1
41	11.69	13.45	13.69	3	4	3
42	11.69	13.33	13.43	4	3	3
43	12.23	13.92	13.98	3	—	—
44	11.85	13.37	13.95	3	—	—
45	11.65	13.39	13.53	3	—	—

Example 46

The purpose of this example is to show the anti-soil redeposition characteristic of the agent of the invention. Unlike the other advantageous characteristics of the agent, there is no industry-accepted or standard test for measurement of soil redeposition. The test employed herein, in general, is the same as the aforesaid home laundering AATCC Test Method 124, using Table I, III Machine, except as noted below. The test is carried out using redeposition soil consisting of, on a weight basis:

Germantown Lamp Black	9.7 parts
Crisco®	29.1 parts
Nujol®	41.8 parts
Wheat starch (screened through a 100-mesh sieve, U.S. Sieve Series)	19.4 parts
Total parts:	100.0

The Crisco® and Nujol® are heated to 38°C and the lamp black and starch are added with stirring at this temperature until a homogeneous mixture is obtained. The redeposition soil is stored under refrigeration until used. The treated fabric samples, prepared as described above, are washed, along with the ballast load fabric. The redeposition soil is added along with the detergent (10 grams of soil are admixed with 50 grams of Tide® commercially available detergent; a paste is formed by admixing in the presence of 100 ml (0.1 x 10^{-3} m³) of 82-93°C water). The soil is uniformly dispersed in the washing machine before the ballast and test samples are introduced. Washing is carried out under the normal wash cycle (12 minutes) using a hot water temperature of 60 ± 3°C. After the test samples are dried, as described hereinabove, they are compared with corresponding unsoiled fabric samples using the AATCC Gray Scale, the higher the evaluation number, the less is the stain. Table V which follows provides soil redeposition data for untreated and treated (with the agent of the invention) fabrics. The soiling procedure was carried out on fabric samples treated with the agent of the invention and on such samples which had been washed 5X and 10X, that is, washed 5X and 10X after application of the agent before being subjected to the soiling procedure. The agent was applied to the fabric, by the procedure already given, with curing in the presence of sodium sulfate/citric acid being carried out for 1 minute at the temperature indicated in the table.

TABLE V

Agent from Ex. No.	Cure Temp. (°C)	Gray Scale Reading		
		I	5W	10W
26*	182	4	3	3
27**	199	5/4	5/4	5/4
28**	199	5/4	5/4	5/4
Untreated fabric* (Control)	—	3	1	1
Untreated fabric** (Control)	—	2	2	2

*white Qiana®
**polyester

Experiments 1 to 5

The following Experiments 1 to 5 are intended to show various compositions which fail to meet the aforesaid requirements of the invention and which, therefore, are outside the invention. Data summariz- ing Experiments 1 to 5 are given in Table VI. The definitions of formula terms and code designations are the same as given above for Examples 1 to 45 (in all cases, X is the same as in said examples, exclud- ing Example 44).

TABLE VI

Expt. No.	(a)	Y_1	(b)	Y_2	(c)	Y_3	HLB	Viscosity (pascal seconds)
1	0	—	0	—	1	G_3	16.8	0.025
2	1	A_1	1.2	A_2	1	A_3	16.1	0.236
3	1	A_1	1.2	A_2	1	A_3	16.1	0.082
4	1	A_1	1	C_2	1	M_3	18.1	1.570
5	1	A_1	1	F_2	1	C_3	18.2	3.700

Expt. No.	A.S.			S.R.		
	I	5W	10W	I	5W	10W
1	12.86	14.08	14.43	1	—	—
2	12.77	15.25	15.73	4	4	3
3	12.41	13.88	14.50	4	2	2
4	12.41	13.61	14.47	3	3	—
5	12.50	13.95	14.96	3	3	2

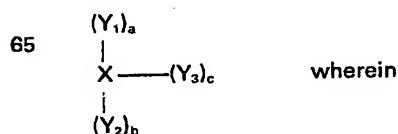## BEST MODE FOR CARRYING OUT THE INVENTION

The best mode for carrying out the invention resides in the embodiments described above wherein the agent of Example 26 is applied by pad application to 6 ounce (0.170 kg) doubleknit fabric of 100% polyester filament, using calcium nitrate in the pad bath, with curing of the agent on the fabric being effected in 0.75 minute at 199°C.

INDUSTRIAL APPLICABILITY

The invention disclosed herein is particularly use- ful for imparting durable, antistatic, soil release characteristics to textile fabric treated with the agent of the invention by the process of the invention.

CLAIMS

1. Process for applying durable, antistatic soil release agent to a substrate, said agent being of the formula

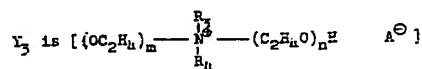$$\begin{array}{c} (Y_1)_a \\ | \\ X——(Y_3)_c \\ | \\ (Y_2)_b \end{array} \quad \text{wherein}$$

X is an aminoplast resin moiety having amino nit- rogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nit- rogen atom and to Y_1, Y_2 or Y_3;

Y_1 is $O(C_2H_4O)_{5-20}R_1$ wherein R_1 is C_{1-5} alkyl;
Y_2 is $O(C_2H_4O)_{6-88}R_2$ wherein R_2 is C_{6-20} alkyl;

$$Y_3 \text{ is } [(OC_2H_4)_m—\overset{\overset{R_3}{|}}{\underset{\underset{R_4}{|}}{N}}{}^{\oplus}—(C_2H_4O)_n{}^{\mathrm{H}} \quad A^{\ominus}]$$

wherein R_3 is C_{4-20} alkyl, C_{4-20} alkenyl or benzyl, R_4 is C_{1-4} alkyl, $A^{\ominus}$ is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;

each of a and b is 0 to 2 and the sum of a and b is 0 to 2;

c is 1 to 2;

the sum of a, b and c is 1 to 4;

said agent having a calculated hydrophile - lipophile balance (HLB) of 14.5 to 18.0, a 20 weight % aqueous solution viscosity, as measured at 20°C on a Brook- field viscometer, of 0.250 to 16,000 pascal seconds, an electrical resistivity (Keithley log R) on polyester fabric, at 20 ± 2% relative humidity and 23 ± 1°C, of no greater than 13.00 initially and no greater than 14.25 after ten washes, and a soil release rating on polyester fabric of at least 3 initially, said process

comprising the steps:

(a) diluting the agent with a normally liquid medium to achieve the desired application liquid viscosity,

5　(b) adding sufficient salt of a mono-, di- or trivalent metal or of an ammonium cation to achieve a cloud point (measured as described herein), of the diluted agent of step (a), of less than 100°C but greater than 25°C, or adding sufficient polyacidic com-

10 pound having a second dissociation constant of greater than 1×10^{-8} to achieve a pH of the diluted agent of step (a) of 3.0 to 6.0, or adding both said salt and said polyacidic compound to achieve said cloud point and pH,

15　(c) applying the diluted agent of step (b) to the substrate to be treated so as to achieve the desired level of agent on the substrate,

(d) drying and curing the agent on the substrate, and

20　(e) recovering substrate which has been durably treated with the agent of the aforesaid formula.

2. Process as claimed in Claim 1 wherein the normally liquid medium is water.

3. Process as claimed in Claim 1 or Claim 2

25 wherein step (b) is carried out by adding only salt and step (c) is an exhaust application step.

4. Process as claimed in Claim 1 or Claim 2 wherein step (b) is carried out by adding only polyacidic compound and step (c) is a pad applica-

30 tion step.

5. Process as claimed in Claim 1 or Claim 2 wherein step (b) is carried out by adding salt and polyacidic compound and step (c) is a pad application step.

35　6. Process as claimed in any of the preceding claims wherein the substrate is a textile fiber.

7. Process as claimed in Claim 6 wherein the substrate is a textile fabric.

8. Process as claimed in Claim 7 wherein the

40 substrate is a polyester textile fabric.

9. Process as claimed in Claim 7 wherein the substrate is a polyamide textile fabric.

10. Process as claimed in Claim 2 wherein the agent in step (a) is diluted as to provide a $\leqslant 20$ weight %

45 aqueous solution of agent.

11. Process as claimed in Claim 10 wherein the substrate is a textile fabric and curing in step (d) is carried out at 149 to 204°C.

12. Process as claimed in Claim 11 wherein the

50 substrate is a polyester textile fabric and curing in step (d) is carried out in 0.25 to 6 minutes.

13. Process as claimed in any one of the preceding claims wherein curing is carried out at 193 to 199°C for 0.25 to 1.25 minutes.

55　14. Process as claimed in any one of the preceding claims wherein the salt is the nitrate, phosphate, chloride, sulfate, oxalate, acetate or citrate of a sodium, magnesium, calcium, zinc, aluminum or ammonium cation.

60　15. Process as claimed in any one of Claims 1 to 13 wherein the salt is calcium nitrate.

16. Process as claimed in any one of the preceding claims wherein the polyacidic compound is phosphoric, citric, oxalic, tartaric, succinic, glutaric

65 or polyacrylic acid.

17. Process as claimed in Claim 16 wherein the polyacidic compound is polyacrylic acid having a molecular weight of up to about 5,000.

18. Process as claimed in any one of claims 1 to

70 13 wherein the salt is sodium sulfate and the polyacidic compound is citric acid.

19. Process as claimed in any one of Claims 1 to 13 wherein the salt is calcium nitrate and the polyacidic compound is citric acid.

75　20. Process as claimed in any one of the preceding claims wherein Y_1 is $O(C_2H_4O)_{10-16}$ and R_1 is CH_3, wherein Y_2 is $O(C_2H_4O)_{15-30}$ and R_2 is $C_{13}H_{27}$, wherein R_3 is C_{8-18} alkyl, R_4 is CH_3, $A^{\ominus}$ is $^{\ominus}OSO_3CH_3$ and $m+n$ is 20 to 50, and wherein X is
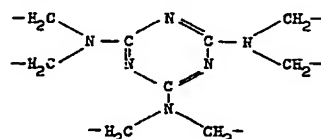
21. Process as claimed in any one of the preceding claims wherein the HLB is 15.5 to 17.0 and the viscosity is 2.000 to 8.000 pascal seconds.

90　22. Process as claimed in any one of Claims 1 to 19 wherein a is greater than 0 in the first general formula set forth in Claim 1.

23. Process as claimed in any one of Claims 1 to 19 or 22 wherein b is greater than 0 in the first gen-

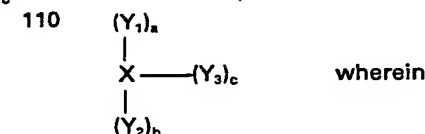95 eral formula set forth in Claim 1.

24. Process as claimed in Claim 23 wherein each of a and b is greater than 0.

25. Process as claimed in any one of the preceding claims wherein the pH in step (b) is 4.0 to 5.5.

100　26. Process for applying durable, antistatic soil release agent to a substrate substantially as described herein with reference to the Examples.
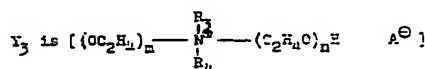
27. Substrates, including textile fibers and fabrics, whenever treated by the process claimed in any

105 one of the preceding claims.

28. A durable, antistatic soil release agent which is resistant to yellowing on the substrate treated therewith and which is of the formula

110
$$
\begin{array}{l}
(Y_1)_a \\
| \\
X\text{——}(Y_3)_c \qquad\qquad \text{wherein} \\
| \\
(Y_2)_b
\end{array}
$$
115

X is an aminoplast resin moiety having amino nitrogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nitrogen atom and to Y_1, Y_2 or Y_3;

120　Y_1 is $O(C_2H_4O)_{5-20}R_1$ wherein R_1 is C_{1-5} alkyl; Y_2 is $O(C_2H_4O)_{5-88}R_2$ wherein R_2 is C_{6-20} alkyl;

$$Y_3 \text{ is } [(OC_2H_4)_m\text{——}\overset{\overset{R_3}{|}}{\underset{\underset{R_4}{|}}{N}}\text{——}(C_2H_4O)_n\text{——} \quad A^{\ominus}]$$

125

wherein R_3 is C_{4-20} alkyl, C_{4-20} alkenyl or benzyl, R_4 is C_{1-4} alkyl, $A^{\ominus}$ is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;

130　each of a and b is 0 to 2 and the sum of a and b is 0

to 2;
  c is 1 to 2;
  the sum of a, b and c is 1 to 4;
  said agent having a calculated hydrophile - lipophile
5 balance (HLB) of 14.5 to 18.0, a 20 weight % aqueous
  solution viscosity, as measured at 20°C on a Brook-
  field viscometer, of 0.250 to 16.000 pascal seconds,
  and electrical resistivity (Keithley log R) on polyester
  fabric, at 20 ± 2% relative humidity and 23 ± 1°C, of
10 no greater than 13.00 initially and no greater than
  14.25 after ten washes, and a soil release rating on
  polyester fabric of at least 3 initially.
    29.   An agent as claimed in Claim 28 wherein Y_1 is
  $O(C_2H_4O)_{10-16}$ and R_1 is CH_3, wherein Y_2 is
15 $O(C_2H_4O)_{15-30}$ and R_2 is $C_{13}H_{27}$, wherein R_3 is C_{8-18}
  alkyl, R_4 is CH_3, $A^{\ominus}$ is $\ominus OSO_3CH_3$ and m + n is 20 to 50,
  and wherein X is

20
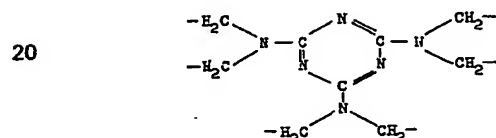
25 30.   An agent as claimed in Claim 28 wherein a is
  greater than 0.
    31.   An agent as claimed in Claim 28 wherein b is
  greater than 0.
    32.   An agent as claimed in Claim 28 wherein
30 each of a and b is greater than 0.
    33.   An agent as claimed in any one of Claims 28
  to 32 wherein HLB is 15.5 to 17.0 and the viscosity is
  2.000 to 8.000 pascal seconds.
    34.   An agent as claimed in any one of Claims 28
35 to 33 dispersed or dissolved in a normally liquid
  medium.
    35.   An agent as claimed in Claim 34 wherein the
  normally liquid medium is water.
    36.   An agent as claimed in Claim 35 dissolved in
40 water to form a ≳20 weight % aqueous solution.
    37.   An agent as claimed in Claims 35 or 36
  wherein the aqueous solution includes a salt of a
  mono-, di or trivalent metal or of an ammonium
  cation.
45 38.   An agent as claimed in Claim 37 wherein the
  salt is the nitrate, phosphate, chloride, sulfate, oxa-
  late, acetate or citrate of a sodium, magnesium, cal-
  cium, zinc, aluminum or an ammonium cation.
    39.   An agent as claimed in any one of Claims 35
50 to 38 wherein the aqueous solution includes a
  polyacidic compound having a second dissociation
  constant greater than 1×10^{-8}.
    40.   An agent as claimed in Claim 39 wherein the
  polyacidic compound is phosphoric, citric, oxalic,
55 tartaric, succinic, glutaric or polyacrylic acid.
    41.   An agent as claimed in Claim 43 wherein the
  polyacidic compound is polyacrylic acid having a
  molecular weight of up to about 5,000.
    42.   An agent as claimed in Claim 35 wherein the
60 aqueous solution includes sodium sulfate and citric
  acid.
    43.   An agent as claimed in Claim 35 wherein the
  aqueous solution includes calcium nitrate and citric
  acid.
65 44.   A substrate which has been treated with an

antistatic soil release agent claimed in any of Claims
28 to 43.
    45.   A substrate as claimed in Claim 44 which is a
  polyester textile fabric.
70 46.   A substrate as claimed in Claim 44 which is a
  polyamide textile fabric.